

MICROWAVE NONLINEAR DIELECTRIC MATERIALS

RAYTHEON

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Report No. 16

Contract DA 36-039-AMC-03389(E)

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Continuation of contract DA 36-039-sc-89126

FINAL REPORT

15 September 1963 - 14 October 1964

U.S. Army Electronics Laboratories

Fort Monmouth, New Jersey

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MICROWAVE NONLINEAR DIELECTRIC MATERIALS

Report No. 16

Contract DA 36-039-AMC-03389(E,
Technical Requirements No. SCL-2101P 18 February 1964

DA Project No. 1C024401A11203

Continuation of Contract DA36-039-scj89126

Final Report

15 September 1963 - 14 October 1964

Object

To conduct research and development
investigation to develop nonlinear
dielectric materials.

Prepared by

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A. Paladino, P. B. Nutter

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1. PURPOSE

It is the purpose of this work to develop and investigate those materials that exhibit the properties of low loss, low dielectric constant, and high nonlinearity required for application at microwave frequencies.

2. ABSTRACT

Microwave nonlinearity and loss tangent data for alumina and stannate-doped ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$) (BST-50) near the Curie temperature are presented. A hot-pressed, annealed sample is included among the above materials. Similar data on alumina- and lanthana-doped ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$) (BST-70), including a hot-pressed, annealed sample are presented. No unusual behavior was observed, and it is concluded that hot-pressing and annealing do little to improve the behavior of mixed titanate ceramics near the Curie temperature.

A BaTiO_3 ceramic doped with two mole percent of lanthana (La_2O_3) exhibited an extrapolated Curie temperature of $+30^\circ\text{C}$. Its nonlinearity and loss at the Curie peak were both comparable to those of BST-50 or BST-70.

Lanthanum additions to SrTiO_3 depressed the Curie temperature by an amount of $30\text{-}40^\circ\text{C}/\text{mole percent lanthanum}$.

The frequency dependence of the loss tangent of BST-50, BST-70, and lanthana-doped BaTiO_3 is seen to deviate strongly from linear dependence near the Curie temperature. The frequency ranges used were 2-4 Gc/sec and 8-12 Gc/sec.

A summary of the four-year contract period is given and some general conclusions drawn.

3. PUBLICATIONS AND CONFERENCES

3.1 Publications

None

3.2 Conferences

Mr. M. Harris, Dr. A. Paladino, and Dr. P. B. Nutter of Raytheon met with Mr. J. Charlton of USAERDL in Waltham on August 4 to discuss the contract.

4. FACTUAL DATA

The work performed this quarter has emphasized microwave non-linearity and loss of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ (BST-50), $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ (BST-70), and lanthana (La_2O_3) doped BaTiO_3 . Measurements of Curie temperature (T_c) were taken in only a few instances, and the Curie constant C was not tabulated.

The temperature dependence of nonlinearity

$$\eta(E, T) = \left[\frac{e(O, T) - e(E, T)}{e(E, T)} \right]$$

was for most samples that reported in the last report: i. e., similar to the dielectric constant. The value of $\eta \max (10^6 \frac{\text{V}}{\text{m}})$, along with the appropriate measured value of loss tangent $\tan \delta$, are reported for each material.

Measurements of $\tan \delta$ vs frequency near T_c are reported in somewhat more detail since those are the first such measurements reported in this series.

4.1 Microwave Nonlinearity and Loss of Doped BST-50 Near the Curie Temperature

4.1.1 Alumina-Doped BST-50

Two series of alumina-doped BST-50 ceramics were fabricated and analyzed this quarter in an effort to duplicate the high nonlinearities near T_c observed in similar material previously.¹ Data on material No. 8354-25 appears in Table I (no undoped standard material was available for measurements).

TABLE I
X-BAND NONLINEARITY AND LOSS FOR BST-50
AND X PERCENT Al_2O_3 NO. 8354-25

X (%)	η_{max} (10^6 V/m)	$\tan \delta$ (10^6 V/m)
3	0.749 (-60°C)	0.176 (-60°C)
5	0.683 (-40°C)	0.196 (-40°C)

The three percent doped material was unusual in that the nonlinearity varied only about ± 20 percent from a value of 0.65 throughout a temperature range of -60°C to -20°C. The Curie peak of this material, as measured at 1 kc, was reasonably narrow ($\sim 20^\circ\text{C}$) and the maximum occurred at -30°C. The nonlinearity of the five percent doped sample showed the usual sharp peak vs temperature.

It should be noted that all microwave measurements published in this report, with the exception of those on lanthana-doped SrTiO_3 , were made using the differentially chopped bias technique.²

Data on a second series of alumina-doped BST-50 ceramics appears in Table II.

TABLE II
X-BAND NONLINEARITY AND LOSS FOR
BST-50 AND X PERCENT Al_2O_3 NO. 8354-34

X (%)	η_{max} (10^6 V/m)	$\tan \delta$ (10^6 V/m)
0	1.07 (8×10^5 V/m) (-30°C)	0.29 (-30°C)
3	1.22 (8×10^5 V/m) (-30°C)	0.230 (-30°C)
5	0.61 (-40°C)	0.186 (-40°C)

The high nonlinearities of the undoped and the three percent doped material were double checked and found to be accurate to within \pm five percent. The nonlinearity for all three materials was quite sharply peaked vs temperature.

4.1.2 Stannate-Doped BST-50

It will be recalled that an earlier report³ concluded that well above T_c , the optimum SrSnO_3 doping in BST-50 was somewhere between one and five mole percent. Two such materials were analyzed recently near T_c . One material showed the above behavior and the other showed nearly the opposite.

A summary of η_{max} (10^6 V/m) and the corresponding $\tan \delta$ for the material designated 8354-26 appears in Table III.

TABLE III
X-BAND NONLINEARITY AND LOSS OF BST-50
AND X PERCENT SrSnO_3 (No. 8354-26) NEAR T_c

X (%)	η_{max} (10^6 V/m)	$\tan \delta$ (10^6 V/m)
0	0.718 (-30°C)	0.122 (-30°C)
3	0.572 (-30°C)	0.091 (-30°C)
5	0.786 (-30°C)	0.144 (-30°C)

η_{max} should be understood to mean the maximum nonlinearity measured at fixed temperature intervals (usually 10°C and sometimes 5°C) in a range including the Curie peak. No attempt was made to find the temperatures where η showed the true maximum.

Table III shows that material No. 8354-26 violates the stannate-doping rule mentioned earlier.

Table IV summarizes the properties near T_c of the second stannate-doped BST-50 material No. 8354-36.

TABLE IV
X-BAND NONLINEARITY AND LOSS OF BST-50
AND X PERCENT SrSnO₃ (No. 8354-36) NEAR T_c

X (%)	η_{\max} (10 ⁶ V/m)	$\tan \delta$ (10 ⁶ V/m)
0	0.491 (-50°C)	0.235 (-50°C)
	[0.450] [(-20°C)]	[0.108] [(-20°C)]
3	0.843 (-50°C)	0.310 (-50°C)
	[0.632] [(-20°C)]	[0.162] [(-20°C)]
5	0.318 (8 kc/cm) (-50°C)	0.116 (-50°C)
	[0.301] [(-20°C)]	[0.087] [(-20°C)]

The bracketed quantities represent the local maximum of η near the Curie peak region. This material is the first measured to date in which the nonlinearity of the upper end of the ferroelectric region exceeds that near the Curie peak, which occurs at the transition to the paraelectric state.

The two stannate-doped materials above were made from the same batch of raw material, calcined, and fired as follows:

No. 8354-26 was fired at 1400°C for 10 hours resulting in a grain size of 5 to 10 microns; No. 8354-36 was fired at 1375°C for 20 hours, resulting in a grain size of 20 to 30 microns. The larger grain size affected η_{\max} very little.

4.2 Microwave Nonlinearity and Loss of Doped BST-70 Near the Curie Temperature

4.2.1 Alumina-Doped BST-70

In a continued effort to achieve a high nonlinearity at room temperature, an alumina-doped BST-70 material was made. This material, designated 8354-64, compares unfavorably with the two similar materials reported last quarter. Unfortunately the undoped standard of batch 8354-64 was not available for microwave analysis. A summary of the three and five percent doped samples appears in Table V.

TABLE V
X-BAND NONLINEARITY AND LOSS OF BST-70
AND X PERCENT Al_2O_3 (No. 8354-64)

X (%)	η_{\max} (10^6 V/m)	$\tan \delta$ (10^6 V/m)
3	0.632 (+20°C)	0.186 (+20°C)
5	0.666 (+20°C)	0.151 (+20°C)

4.2.2 Lanthana-Doped BST-70

A BST-70 material with one-half percent La_2O_3 showed a nonlinearity of $\eta_{\max} (10^6 \text{ V/m}) = 0.79$ and a loss tangent $\tan \delta (10^6 \text{ V/m}) = 0.21$ at + 20°C. This material broke down electrically several times and further work was stopped.

4.3 Microwave Nonlinearity of Lanthana-Doped BaTiO₃ Near the Curie Temperature

It has been reported⁴ that lanthana (La₂O₃) additions to BaTiO₃ ceramics lower the Curie temperature dramatically. It was determined by x-ray techniques that the lanthanum ion substitutes for barium in the fashion La_xBa_{1-x}TiO₃; values of x of 0.05 dropped the Curie temperature by 100°C, and lower values of x decreased T_c proportionally less.

This drop in T_c is thought to be due to a combination of size and valence mismatch of the lanthanum ion in the barium site of the BaTiO₃ structure. The Lattice potential is thus greatly disturbed and it was hoped that high nonlinearities might be a correlary result of the modified potential. In addition, the low percent doping (~ 4 to 5) acquired to bring the Curie temperature near room temperature might reduce the so-called impurity scattering loss. In view of the drastic effect on Curie temperature, however, not much hope was held out for a reduction in losses because of a probable increase in fourth order anharmonic scattering loss.

A number of one, two, and four percent lanthanum-doped BaTiO₃ samples ($\frac{1}{2}$, 1, and 2 percent La₂O₃, respectively) were prepared. The one percent lanthanum samples were laminar in structure, very porous, and crumbled when cut with a diamond saw or ultrasonic tool. The two percent samples were by contrast extremely hard and dense materials - excellent ceramics in the mechanical sense - and were colored olive drab. The four percent samples were nearly as good.

These materials (including a few one percent doped samples that survived machining) were prepared in the usual manner and run in the X-band test setup (differently chopped bias). In most cases, no response at all was observed over a wide range of temperature and bias. This implies either a very high loss tangent (tan δ of 0.5 or more) or a very low nonlinearity. Two materials showed

some response at high values of bias, but not enough above noise to confidently report η and $\tan \delta$. Only one material ($\text{BaTiO}_3 + 2\% \text{La}_2\text{O}_3$, No. 8354-79) gave strong response so that measurements could be made.

This material had $\eta_{\text{max}}(8 \times 10^5 \text{ V/m}) = 0.58$ at $+50^\circ\text{C}$. This was a sharply peaked maximum, the values $\eta(8 \times 10^5 \text{ V/m})$ being 0.155 and 0.232 at 40° and 60°C respectively. The Curie peak in the plot of ϵ vs T at 1000 cps was also much sharper than in mixed titanates. The loss tangent $\tan \delta$ at $+50^\circ\text{C}$ was 0.185.

The extrapolated Curie temperature of material No. 8354-79 was about $+30^\circ\text{C}$.

4.4 Microwave Nonlinearity of Lanthanum-Doped SrTiO_3 Above the Curie Temperature

Additions of LaAlO_3 were made to SrTiO_3 ceramics to see whether the effect on T_c was similar to that in BaTiO_3 . The Curie point depression was in fact a little stronger, being $30\text{-}40^\circ\text{C}/\text{mole percent La}$. The S-band nonlinearity at liquid nitrogen temperature (77°K) was accordingly small for doped samples. The results are tabulated in Table VI.

TABLE VI

S-BAND NONLINEARITY OF SrTiO_3 AND
X PERCENT LaAlO_3

Material	X	$T_c, ^\circ\text{C}$	$\eta(10^6 \text{ V/m}, 77^\circ\text{K})$
(8354-30)	1	-269	0.023
	2	-291	0.009
(8354-37)	0	-225	0.082
	1	-278	0.021
	2	-306	0.012

These measurements were taken with a slab line sample in a coaxial S-band test setup. No loss data was taken. The accuracy of the extrapolated Curie temperatures are no better than $\pm 5^\circ\text{C}$ since no data was taken below 77°K (-196°C).

4.5 Frequency Dependence of the Loss Tangent of BST-50, BST-70, and Lanthana-Doped BaTiO₃

The frequency dependence of the loss tangent of SrTiO₃ single crystal has been reported as being linear.⁵ The measurements were taken in a temperature range from -175°C to -150°C , in a frequency range from 2.4 to 6.6 Gc/sec, and with an applied field of 18.3 kV/cm in the (100) direction. The Curie point (extrapolated) of the SrTiO₃ sample was -237°C .

Despite the limited nature of this data, linear frequency dependence of loss tangent has been assumed for all ferroelectric materials, pure and mixed, single crystal and ceramic, at temperatures well above T_c . Usually, the frequency range involved is quite small, e. g., 18-22 Gc/sec for K-band measurements, and the loss data is "normalized" to a given frequency, say 21 Gc/sec, more for the sake of form than for extreme accuracy.

Recent measurements of the nonlinearity and loss of BST-50 and BST-70 ceramics near T_c have shown⁶ that efficient ferroelectric switches for 1.2 Gc/sec may be possible if the loss tangent is proportional to frequency. (Our measurements were taken in the range 8-12.5 Gc/sec.) Hence, measurements of $\tan \delta$ vs frequency over an extended range are of paramount importance at this time.

Equipment for an S-band experiment (1.9 to 4.0 Gc/sec) in coaxial cable was setup in a manner as nearly identical as possible to that

used at X-band. The sample holder was inserted into a Microline 352 B coaxial adapter to effect the same degree of loose coupling as in the X-band sample holder.⁷ The sample was not electrically connected to the center conductor so that the (comparatively) high coupling of the slab line configuration, often used in coax, was avoided.

The detection scheme used at S-band was identical to that used at X-band, i. e. , differentially chopped bias.

Electroded samples of BST-50, BST-70, and lanthana-doped BaTiO_3 were successively checked out at fields of approximately 0, 4, 8, and 12 kV/cm, and at various temperatures from the Curie point up. The field dependence of the loss was verified as being slight in the ferroelectric-paraelectric transition region (Curie peak). In some of the data to follow, both frequency and electric field are different, but the latter can be ignored to obtain the qualitative frequency dependence of loss tangent.

The data for the three materials are summarized in Tables VII, VIII, and IX.

For BST-50, the loss appears to exhibit a roughly linear frequency dependence at the highest temperature measured. As the temperature is dropped, the frequency dependence becomes less and less marked so that near the Curie peak ($\sim -34^\circ\text{C}$) there is essentially no difference in loss tangent in a four to one frequency range.

The data for BST-70 and lanthana-doped BaTiO_3 shows similar behavior except that the S-band loss near the Curie peak exceeds the X-band loss, in several instances by as much as a factor of two.

TABLE VII

LOSS TANGENT VS FREQUENCY FOR BST-50 No. 8354-34
(Thickness = 10.5 Mils)

<u>T</u> <u>(°C)</u>	<u>V_{dc}</u> <u>(V)</u>	<u>f_o</u> <u>(Gc/sec)</u>	<u>tan δ</u> <u>(×10³)</u>
+20	27	10.02	46.5
	295	3.11	22.3
+20	115	9.38	44.4
	115	2.75	31.5
	295	9.85	47.6
	295	2.87	36.2
+8	205	8.78	51.3
	295	9.03	53.8
	295	2.60	53.4
-7	295	2.39	43.5
-14	27	9.28	99.8
	295	2.36	95.6
	295	3.73	111
-28	295	9.04	130
	295	2.50	139
-34	295	9.40	133
	295	2.69	155

TABLE VIII

LOSS TANGENT VS FREQUENCY FOR BST-70 No. 8354-38

(Thickness = 8.3 Mils)

<u>T</u> <u>(°C)</u>	<u>V_{dc}</u> <u>(V)</u>	<u>f_o</u> <u>(Gc/sec)</u>	<u>tan δ</u> <u>(× 10³)</u>
+80	210	8.61	66
	210	3.17	44
	120	8.44	59.5
+70	210	8.23	80
	210	2.80	31
+66	210	11.36	87
	210	2.57	94.5
+50	210	10.85	118
	210	2.50	111
	120	9.83	116
	120	2.11	139
+40	210	10.92	165
	210	2.63	231
+25	210	10.57	106.5
	210	3.73	102
	120	9.71	148
	120	3.18	212
+10	120	11.18	141
	120	2.11	164

TABLE IX
LOSS TANGENT VS FREQUENCY FOR BaTiO₃ AND
TWO PERCENT La₂O₃ No. 8354-79
(Thickness = 11.0 Mils)

<u>T</u> <u>(°C)</u>	<u>V_{dc}</u> <u>(V)</u>	<u>f_o</u> <u>(Gc/sec)</u>	<u>tan δ</u> <u>(× 10³)</u>
+80	210	11.30	111
	210	2.69	238
+70	210	10.91	159
	210	2.63	284
+60	210	11.08	153
	210	2.69	277
+40	210	9.47	176
	210	3.33	214
+30	210	9.90	215
	120	3.24	241

No account of skin or other extraneous losses has been taken in this data. If an amount of 10×10^{-3} is subtracted off to account for this loss, the frequency dependence well above the Curie peak becomes more nearly linear, while that near the Curie peak is affected very little. Actually this type of correction takes no account of frequency dependence of skin loss, eddy current loss, etc., and hence is not quantitative. It does indicate that the qualitative behavior of these materials near the Curie peak has been properly established.

5. CONCLUSIONS

5.1 Nonlinearity and Loss Near the Curie Temperature

Our continued measurements of microwave nonlinearity and loss near T_c tend to bear out the general conclusion reached in the previous report; i. e., that materials of large grain size tend to exhibit higher nonlinearity than those of smaller grain size. In addition, the loss tangent is comparable for the two types of materials although the density and machining properties of large grain materials tend to be inferior to those with smaller grains. These remarks appear to be applicable to BST-50 and BST-70 ceramics; since too little time was available for scientific investigation of the effect of grain size, our findings should be taken at face value.

Although a lanthana-doped sample of BaTiO_3 ceramic was shown to have nonlinearity and loss in the Curie region comparable to BST-50, the reader is reminded that most samples exhibited no signal when analyzed using the differentially chopped bias method. This most likely indicates high losses ($\tan \delta > 0.5$ or more) although it might indicate very low nonlinearity. The outlook on this doping cannot be determined without a further study of the effect of lanthana upon the losses of BaTiO_3 . At the present, no means exist for such investigation in the Curie peak region.

5.2 Losses Versus Frequency

The observed behavior of $\tan \delta$ versus microwave frequency near the Curie temperature can be roughly correlated with the findings of Stanford.⁸¹ He measured the real part of the dielectric constant of BST-80 versus frequency and temperature (from the Curie peak downwards) and found evidence for a dielectric constant resonance in the general region of S-band. Such a resonance is usually accompanied by a peak in loss tangent so that X-band frequencies would be on the high side of the loss peak.

Although our measurements covered a limited frequency range, the results indicate that BST-50, BST-70, and lanthana-doped BaTiO₃ will be no more suited for device application at S-band than at X-band if operated in the ferroelectric region. Operation at very low or very high microwave frequencies is not ruled out, since one may be able to get far enough away from the loss peak to obtain acceptably low losses. It is to be expected that the nonlinearity at very high frequencies will be reduced, however, since the dielectric dispersion will have reduced the field-free dielectric constant. It might be fruitful to investigate nonlinearity and loss of ferroelectrics in the frequency range of 0.5-1 Gc/sec.

6. SUMMARY OF FOUR-YEAR CONTRACT PERIOD

Raytheon work on nonlinear microwave dielectric material sponsored by the U. S. Army Signal Corps has extended over a four-year period. During this time the state of the art has come from essentially first principles to the present state, which might be described as materials engineering. Also, there have been numerous side avenues opened up temporarily and an unavoidable amount of backtracking.

It is the purpose of this section first to summarize the first three years of work; subsequently, the past year's work will be summarized and some over-all conclusions drawn.

6.1 The Period September 1960 - September 1963

6.1.1 September 1960 - September 1961 (Contract No. DA 36-039-SC-87369) *

The material of greatest theoretical and practical interest was SrTiO_3 above the 110°K phase transition. The work for this contract was to a large extent, based on the results of earlier work^{8, 9} performed for Air Force Cambridge in this laboratory. The latter research will not be detailed here, but its results will necessarily be interwoven with the findings of the 1960-61 Signal Corps contract work. In addition, Slater's theory of ferroelectricity¹⁰ published in 1950 served as a guidepost for the later (and more consistent with experiment) understanding of the temperature dependence of dielectric constant and nonlinearity of SrTiO_3 .

The theoretical and experimental work on SrTiO_3 were very closely knit together. The experimental dependence of dielectric constant ϵ upon applied electric field E had been found to be^{8, 11}

$$\frac{\epsilon(E)}{\epsilon(O)} = \frac{1}{1 + \frac{A_{hkl}}{C} \epsilon^3(O) E^2}$$

* Reports No. 1-4 of this Series published under this contract number.

where $C =$ Curie constant

$A_{hkl} \equiv$ nonlinearity constant for SrTiO_3 .

Experimentally A_{hkl} had been found to be temperature- and frequency-independent, but did depend upon the direction of the applied field E with respect to the cubic axes of SrTiO_3 (thus the subscripts hkl). The Slater theory¹⁰ predicted this behavior; the value of A_{100} for SrTiO_3 calculated on the Slater theory was 4.2×10^{-18} ($^\circ\text{C m}^2/\text{volt}^2$) versus an experimental value of 1.15×10^{-18} . The Slater calculation assumed that nonlinearity was caused by the titanium ion "rattling" in the surrounding oxygen octohedron. If instead one calculates A_{100} by assuming a vibration of the strontium ion towards the TiO_3 complex,¹¹ the result is 2.2×10^{-18} . The basic result of the Slater theory, that A_{hkl} is proportional to the ionic polarizability α of the essential ion, indicates that no miracles can be expected in improving the nonlinearity of perovskite type materials.¹¹

The microwave losses of SrTiO_3 had been investigated prior to this contract work. The field and temperature dependence of $\tan \delta$ had been observed experimentally. The temperature dependence of $\tan \delta$ was treated theoretically in 1960-61.

Microwave losses were believed due to excitation of the transverse mode of uniform polarization by the microwave field, and decay of this mode into other lattice modes. The complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ may be written¹¹

$$\epsilon = \frac{A}{\Omega_T^2 - \omega^2 + i\gamma}$$

$$\approx \frac{A}{\Omega_T^2} - i \frac{A\gamma}{\Omega_T^4}$$

where A is a constant,

Ω_T is the frequency of the uniform mode,

ω is the microwave frequency ($\omega \ll \Omega_T$),

and γ is a damping factor ($\gamma \ll \Omega_T^2$ for low-loss samples).

Since the temperature dependence of Ω_T was known⁸ to be $\Omega_T \sim \sqrt{T - T_c}$, where T_c is the Curie temperature of SrTiO_3 , the loss tangent $\tan \delta = (\gamma/\Omega_T^2) \sim (\gamma/T - T_c)$.

The temperature dependence of γ is different depending on the loss mechanism. Scattering by an impurity was shown to result in a temperature-independent γ . An n th order anharmonic interaction contributes a loss characterized by $\gamma \sim T^{n-2}$.

The experimental values of $\tan \delta$ for SrTiO_3 could be approximately characterized by¹¹

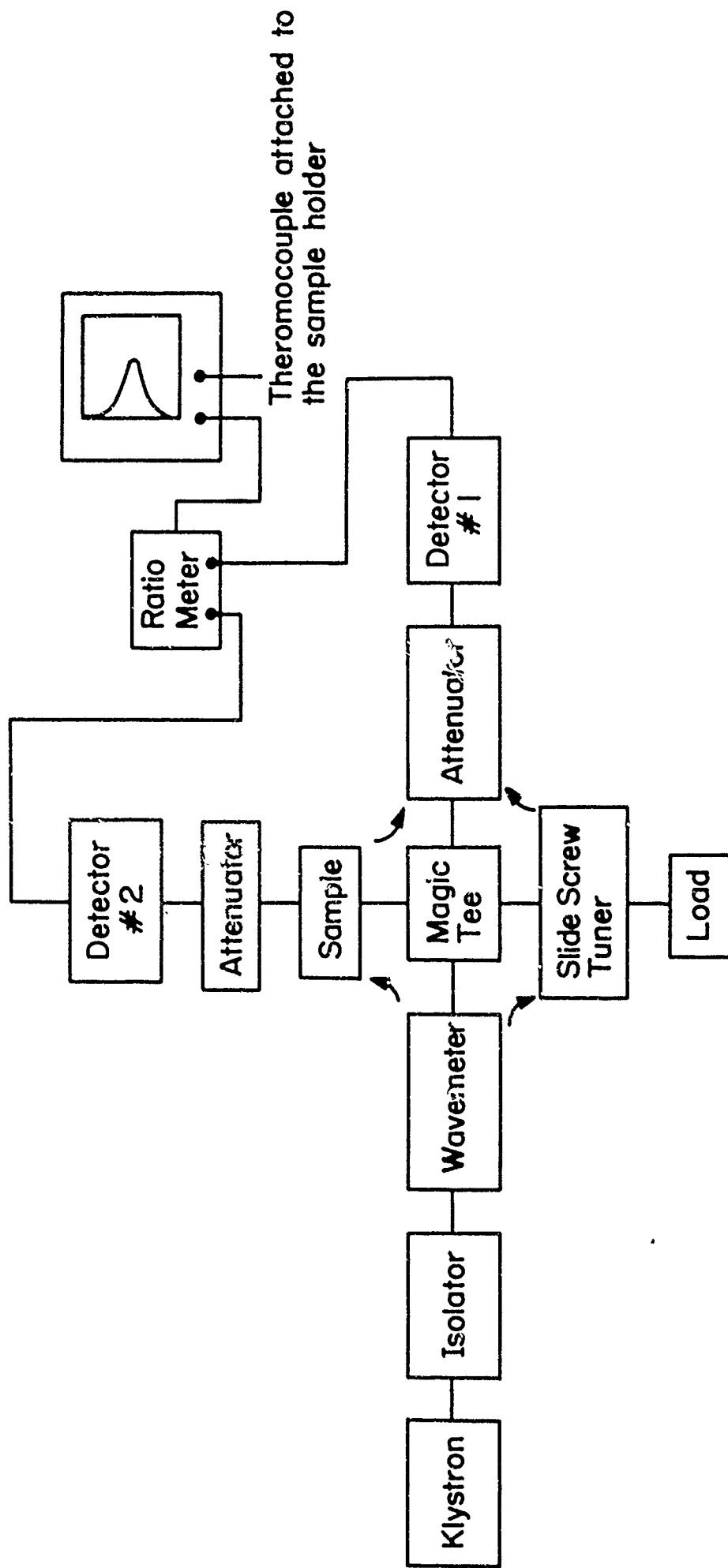
$$\tan \delta = \frac{B}{T - T_c} + \frac{DT^2}{T - T_c}$$

with $B = 7.0 \times 10^{-2} (^\circ\text{K})$ and $D = 3.6 \times 10^{-6} (^\circ\text{K})^{-1}$.

An important test of this relatively simple theoretical description of $\tan \delta$ was to apply it to mixed (Ba, Sr) TiO_3 ceramics and single crystals. Before discussing the results of these experiments, it is perhaps appropriate to review the experimental techniques developed for measuring the loss tangents of high dielectric constant, low-loss materials such as SrTiO_3 at microwave frequencies.^{12, 13, 14}

A small regular-shaped (cube, parallelepiped or sphere) sample of a material obeying the Curie-Weiss law ($\epsilon = C/T - T_c$) is inserted into some polyfoam which in turn is placed in one arm of a waveguide bridge (see Fig. 1). Due to its high dielectric constant the sample can support resonances which can be detected by balancing the bridge off resonance. The temperature of the sample is varied over a wide range while the microwave frequency is kept constant.

Thus, at various temperatures the sample will resonate, i. e., when the dielectric constant ϵ is such as to satisfy the resonance boundary conditions for the given geometry and frequency. Due to losses in the sample,



EXPERIMENTAL SETUP FOR THE MEASUREMENT OF THE LOSS
TANGENT AT K-BAND

FIGURE 1

the resonance will extend over a small interval in ϵ , and this interval corresponds to a temperature interval determined by the Curie-Weiss behavior $\epsilon = C/(T - T_c)$. If numerous resonances are found, C and T_c can be calculated from the resonance temperatures and the known mode chart appropriate for the sample shape. Knowing C and T_c , one may then calculate $\tan \delta$ from the temperature widths of the various resonances.

Returning to the description of $\tan \delta$ vs temperature, Table X shows the results¹⁵ of variously prepared ceramic samples of SrTiO_3 , BST-20, and BST-50. These data may be summarized as follows:

- (a) the constant D in the expression for $\tan \delta$ (the fourth-order anharmonic scattering term) appears not to depend on the (Ba, Sr) ratio, and may thus be thought of as a characteristic of the perovskite lattice;
- (b) the values of B for BST-20 and BST-50 are about ten and thirty times that value for SrTiO_3 , respectively; (c) B varies only slightly with preparation technique, and D not at all. The absence of a D value for the BST-50 ceramics is due to the preponderance of the first loss term in the available temperature range (up to 350°C).

Conclusion (b) at this point of the work could indicate one of two possibilities. The first is that the barium ions act like impurity scatterers in the host SrTiO_3 lattice; in this event, there would be little hope of improvement in losses either through more sophisticated ceramics techniques or by production of mixed (Ba, Sr) TiO_3 single crystals. The second possibility is that scattering due to the presence of grain boundaries (whose magnitude and temperature dependence were unknown at this time) might have been mistakenly assimilated into the constant B , which is supposed to represent impurity scattering only.

In order to resolve the impurity and grain boundary scattering components of the microwave loss tangent, the growth of single crystal (Ba, Sr) TiO_3 was pursued in the hopes that the dependence of loss tangent upon annealing (which influences grain boundary scattering) would determine the relative strength of the two loss mechanisms.

TABLE X

THE LOSS TANGENT OF BARIUM-STRONTIUM TITANATES FOR VARIOUS HEAT TREATMENTS AT 22.0 kMc/se

Material	Heat Treatment	Tan δ *
SrTiO ₃ (Single Crystal)	No Heat Treatment	$\frac{0.069}{T-T_c} + \frac{3.5 \times 10^{-6} T^2}{T-T_c}$
BST-20 Mold	Fired to 1500°C - no soak	$\frac{0.88}{T-T_c} + \frac{3.5 \times 10^{-6} T^2}{T-T_c}$
BST-20 Mold	Fired to 1500°C - 10 hr soak in O ₂	$\frac{0.82}{T-T_c} + \frac{3.5 \times 10^{-6} T^2}{T-T_c}$
BST-20 Hot Press	Fired to 1500°C - no soak	$\frac{0.80}{T-T_c} + \frac{3.5 \times 10^{-6} T^2}{T-T_c}$
BST-50 Mold	Fired to 1500°C - no soak	$\frac{2.76}{T-T_c}$
BST-50 Mold	Fired to 1500°C - 10 hr soak in O ₂	$\frac{2.39}{T-T_c}$
BST-50 Hot Press	Fired to 1500°C - no soak	$\frac{2.34}{T-T_c}$
BST-50 Hot Press	Fired to 1500°C - 10 hr soak in O ₂	$\frac{2.54}{T-T_c}$
BST-50 Hot Press, Ball Milled	Fired to 1300°C - 6½ hr soak in O ₂	$\frac{2.27}{T-T_c}$
BST-50 Hot Press, Ball Milled	Fired to 1500°C - 6½ hr soak in O ₂	$\frac{1.58}{T-T_c}$

*For BST-50, T_c = -223°K; for BST-20, T_c = -105°K; and for SrTiO₃, T_c = -38°K.

Single-crystal SrTiO_3 grown from a KF flux had been prepared early in this contract work.¹⁶ Crystals up to 2.5 mm on an edge were made from runs started at 1200°C and cooled at rates of 2° to 9°C per hour down to 800°C, with more rapid cooling to room temperature. The lattice constant was checked by x-ray diffraction and found to be that of commercial SrTiO_3 single crystal. At the same time, initial attempts to grow BST-50 single crystals by the same technique produced one-millimeter crystals whose mole percent of barium was found to be 66-70 percent by x-ray diffraction techniques.

Numerous starting compositions of $(\text{Ba}, \text{Sr})\text{TiO}_3$ material and KF flux were used in a continuing effort to grow single crystals.¹⁷ Cubes of material 5 mm on a side were obtained, but closer inspection revealed that they consisted of numerous small single crystals of varying (Ba, Sr) ratio. As the melt cools from 1200°C, this ratio favors the barium more and more.

Attempts were begun¹⁷ to seed the saturated solid solution melt with BaTiO_3 and SrTiO_3 single crystals, and cubes of polycrystal $(\text{Ba}, \text{Sr})\text{TiO}_3$ were formed on the seed. Apparent single-crystal areas were separated and their composition determined both by x-ray diffraction measurements of the lattice constant and by measuring the Curie temperature. The two methods gave fairly good agreement on the composition.

In order to reduce the compositional variation of $(\text{Ba}, \text{Sr})\text{TiO}_3$ single crystals, the platinum crucible containing the melt was removed from the furnace at 1050°C.¹⁸ This procedure produced crystals of more uniform composition but reduced the size of the crystals to about 1 mm.

Cadmium niobate single crystals and ceramics were produced towards the end of this contract period¹⁹ but this material was not evaluated as to nonlinearity and loss tangent.

Measurements of the nonlinearity constant $\langle A \rangle$ of various BST ceramics showed little deviation from that of single-crystal SrTiO_3 , or more precisely, the weighted average over all directions of the nonlinearity constant of SrTiO_3 .²⁰ This indicated that $\langle A \rangle$ is characteristic of the perovskite lattice primarily; since $\langle A \rangle$ is related to fourth order anharmonic potential terms in the lattice; this result is consistent with the earlier finding¹⁵ that the loss factor D did not vary with (Ba, Sr) ratio.

Concurrent with the development and evaluation of ferroelectric materials, a ferroelectric phase shifter was developed.²¹ The goals of design were, briefly: (a) 180° of phase shift at 4 to 5 kMc with an applied voltage less than 1 kV, (b) type-N coaxial input and output connectors, and (c) input $\text{VSWR} < 2$. The device produced phase shift through the nonlinearity of a BST-50²² or SrTiO_3 ^{21, 23} loaded TEM transmission line. Severe matching problems were encountered due to the high dielectric constant of the ferroelectric material, but were adequately solved by means of TiO_2 and Al_2O_3 matching transformer sections. Skin losses from the conductive planes of the TEM line were the limiting loss of the phase shifter.

In over-all performance, the BST-50 phase shifter gave 275° phase shift for 1000 volts applied at 0°C with $\text{VSWR} < 2$ and insertion loss = 20 dB,²² the SrTiO_3 phase shifter gave 165° phase shift for 1000 V applied at 88°K with $\text{VSWR} < 1.5$ and insertion loss = 4.5 dB.

6.1.2 September 1961 - September 1962
(Contract No. DA 36-039-SC-89126) *

A continued effort²⁴ to produce single crystals of mixed $(\text{Ba}, \text{Sr})\text{TiO}_3$ solid solutions by the flux technique resulted in crystals three to four mm on an edge in any desired composition. The method of initial preparation has been described earlier.^{16, 17} The badly strained crystals

* Reports No. 5-12 of this Series published under this contract number.

were then annealed for 10 hours at temperatures from 1000° to 1800°C to relieve strains; however, from 1700°C upwards there were distinct signs of melting and recrystallization. The microwave losses of these annealed crystals were about the same as the corresponding polycrystalline material.

Single crystals of SrTiO_3 , doped with small amounts of SrHfO_3 and SrGeO_3 , were grown in sizes up to 7 mm on an edge from KF flux;²⁵ BaTiO_3 single crystals with small amounts of BaHfO_3 were also grown. These crystals were grown to study the effects of small dopants upon microwave nonlinearity and loss.

Single crystals of $\text{Cd}_2\text{Nb}_2\text{O}_7$ up to one-fourth inch on a side were grown from KF flux.²⁶ The optimum molar ratio between $\text{Cd}_2\text{Nb}_2\text{O}_7$ and KF, in regard to crystal size and purity, was between 3.0 and 3.5 to 1. Soaking temperature was quite critical in determining the number of nuclei growing into larger crystals; 1200°C was found to be a good soak temperature for the optimum molar ratio mentioned above.

Single-crystal KTaO_3 was grown by heating K_2CO_3 and Ta_2O_5 in stoichiometric ratio above the melting point ($\sim 1360^\circ\text{C}$) and cooling slowly.²⁷ No flux was necessary for this low-melting crystal.

It will be remembered that one motivation for pursuing single-crystal growth was the hope of determining the role of Ba^{++} ions in contributing to the microwave losses of SrTiO_3 doped with BaTiO_3 . The bulk of the loss analysis was done under a concurrent Air Force Contract,²⁸ but one very important result was found and reported under the Signal Corps contract.²⁹ A single crystal of SrTiO_3 with a one-mole percent addition of BaO was prepared and its loss tangent at 22.0 Gc/sec was fitted by the expression

$$(T - T_c) \tan \delta = \alpha + \beta T + \gamma T^2$$

with $\alpha = 0.034^\circ\text{K}$, $\beta = 6.53 \times 10^{-4}$, and $\gamma = 2.54 \times 10^{-6} (\text{K})^{-1}$. By comparison, for pure SrTiO_3 , $\alpha = 0$, while for $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, $\alpha = 0.62$, with both materials having the same value of β and γ as above. This result was interpreted to mean that Ba^{++} acts like an impurity scatterer which increases the loss tangent approximately proportional to its concentration. There is no longer the possibility that grain boundary scattering alone can account for the increase of microwave losses in mixed (Ba, Sr) TiO_3 over the values for pure SrTiO_3 . This result had been suspected previously, but the above experiment was the first clear proof. *

At the beginning of this section the continued investigation of (Ba, Sr) TiO_3 single-crystal growth was mentioned. This work was pursued throughout the period 1961 - 62 and resulted in a rather complete understanding of crystal growth by recrystallization from flux in the BaTiO_3 - SrTiO_3 - KF system.³⁰ As an aid to the study of crystal growth, the phase diagram for this system was determined experimentally; one result of major importance was obtained from the phase diagram; namely, the path of recrystallization giving a constant (Ba, Sr) ratio. In addition, seeding and certain modifications taking advantage of the natural convection in the crucible were investigated to improve crystal size and uniformity.

As part of the general interest in materials related to SrTiO_3 , numerous solid solution systems of ceramics were investigated and analyzed as to lattice parameter and microwave and audio frequency dielectric constant, nonlinearity, and loss. Only the major results can be listed here.

* In Section 6.1.1 no β term appears in the expression for $\tan \delta$ because at that time the experimental data was not as complete or accurate as it later became. In Reference 14, β and α are shown to be related to third- and fourth-order anharmonic scattering respectively.

The system $\text{SrTiO}_3 - \text{SrSnO}_3$ was found to form a complete solid solution regardless of (Ti, Sn) ratio.³¹ In order to produce dense ceramics without laminations, hydrostatic pressing at room temperature at 30,000 psi was employed. Otherwise the preparation used normal ceramic techniques.

The system $\text{BaHfO}_3 - \text{SrHfO}_3$ also formed a complete solid solution as indicated³² by x-ray data. The dielectric constant at 1 kc was between 27 and 34 from 77°K to room temperature, showing no peaks.

Measurements of the nonlinearity constant A of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ ceramics with $x = 0.1, 0.2$, and 0.3 showed a fairly strong temperature dependence.³³ For example, BST-10 ($x = 0.10$) had $A(T - T_c = 65^\circ\text{K}) = 2.1 \times 10^{-18}$, while $A(T - T_c = 43^\circ\text{K}) = 3.7 \times 10^{-18}$ ($^\circ\text{K meter}^2/\text{volt}^2$). This is in sharp contrast to the temperature independence of A in SrTiO_3 , and casts some doubt upon the usefulness of A in describing the nonlinear behavior of mixed titanates.

The system $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ was found³⁴ to form a solid solution. The addition of Ca^{++} monotonically lowered the dielectric constant from that of SrTiO_3 except at -120°C where the behavior of dielectric constant versus x was complicated. The behavior was correlated with an anomaly of lattice parameter versus x , at the same temperature.

The system $\text{SrSn}_x\text{Ti}_{1-x}\text{O}_3$ showed a monotonic decrease of dielectric constant with x , and no anomaly was observed in this system.³⁴ The system $\text{BaHf}_x\text{Ti}_{1-x}\text{O}_3$ showed similar behavior with x except that the addition of nonferroelectric BaHfO_3 reduced the transition temperature quite drastically.³⁵ The system $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Hf}_x\text{Ti}_{1-x}\text{O}_3$ showed similar behavior.³⁵

Microwave losses of single crystal and polycrystal $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ annealed samples were measured,³⁶ those of the single crystal material had microwave losses described by

$$(T - T_c) \tan \delta = \alpha + \beta T + \gamma T^2$$

with $\alpha = \alpha_0 x (1-x)$ (β and γ the same for single and polycrystal).

The "impurity scattering" term α is thus proportional to the concentration of host ions and of impurity ions. In the region of $x = 0.5$, the best values of α for the annealed polycrystal BST-50 samples were about twice that for the best annealed single crystals, which indicates that improved ceramic techniques might reduce the losses of BST-50 by up to a factor of two.

A solid solution of BST-50 with an impurity addition of one mole percent SrSnO_3 showed a nonlinearity³⁷ constant $A = 29 \times 10^{-18}$ for $E = 2.7 \text{ kV/cm}$ and $A = 5.9 \times 10^{-18}$ for $E = 5.4 \text{ kV/cm}$. These values, taken at 1 Mc/sec , compare with $A = 1.1 \times 10^{-18}$ for undoped BST-50. A measurement at 2.5 Gc/sec showed³⁸ $A = 1.8 \times 10^{-18}$ for the doped material. Two conclusions were drawn from these data: (a) the nonlinearity mechanism in doped BST-50 is different for microwave and 1 Mc/sec frequencies; (b) the nonlinearity constant A is temperature-, frequency-, and field-dependent, and should perhaps not be used to characterize mixed perovskite materials.

One percent CaTiO_3 was added to a BST-50 solid solution³⁷ and showed no definite change in nonlinearity from the undoped BST-50.

It will be remembered that in the previous section the nonlinearity constant A_{100} for SrTiO_3 calculated using Slater's theory of ferroelectricity was about four times higher than the experimental value of $1.15 \times 10^{-18} (\text{°K})$. This calculation assumed that nonlinearity was a result of the Ti^{4+} ion "rattling" in its surrounding oxygen octahedron. If instead one uses Slater's³⁹ suggestion that the normal vibrations of the cation (Sr^{++} in TiO_3) with respect to the TiO_3 complex produce nonlinearity, one obtains the value $A_{100} = 2.2 \times 10^{-18}$. This improved agreement is encouraging but does not firmly identify the correct "soft mode," or temperature-dependent mode. One way to resolve between the two types of suggested modes is to substitute for Sr^{++} in the SrTiO_3 host structure and observe the effect upon microwave dielectric constant.

Such a study was initiated⁴⁰ early in the 1961-62 contract period. X-band measurements of dielectric constant for SrTiO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, and BaTiO_3 were taken up to 820°C in temperature.⁴¹ The data could be accurately expressed as

$$\epsilon = \epsilon_1 + \frac{C}{T - T_c}$$

in all cases, where ϵ_1 is a constant (its significance will be discussed later). CaTiO_3 and $\text{Ca}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ were similarly analyzed,⁴² as was KTaO_3 in the last quarter.⁴³ The values of ϵ_1 , C , and T_c for these materials are tabulated in Table XI. It is clear that cation substitutions affect the values of C and T_c quite strongly, and this suggests that the Sr^{++} vibrations are the source of ferroelectric behavior in SrTiO_3 . ϵ_1 is thought to result from the interaction with the microwave field of two optically active temperature-independent modes characteristic of the perovskite structure and independent of cation substitution.⁴⁴

Last had observed two temperature-independent modes in BaTiO_3 , SrTiO_3 and other perovskites³⁹ and assigned these to the normal vibrations of the TiO_3 group. He further had postulated a third vibration, lower in frequency than the two observed modes, and suggested that a cation-vs TiO_3 vibration was the source of this lowest mode. This last mode was of course thought to be the "soft" or temperature dependent mode.

It should be mentioned that Last's measurements were limited to the frequency range of 1000 to 300 cm^{-1} . Spitzer et al. were able to extend the frequency range to 5000 to 70 cm^{-1} in taking infrared reflectivity measurements on BaTiO_3 , SrTiO_3 and TiO_2 .⁴⁵ They found all three allowed vibrations in BaTiO_3 and SrTiO_3 , of these modes, only the highest one corresponded to one of those reported by Last. Spitzer et al. discuss a possible reason for this discrepancy in some detail.⁴⁵

On the basis of calculated resonance strengths for the observed vibrational modes, Spitzer et al. concluded that the low frequency mode was a normal vibration of the TiO_3 group, in contrast to Last's conclusion. In addition, Spitzer's calculated resonance strengths for the two higher frequency modes indicated that these two modes alone could not account for our observed values of ϵ_1 .⁴⁶

It should be noted that the mode assignment of Spitzer et al. was only semi-quantitative, and it is possible that the soft mode is a combination of the two types of vibrations mentioned above.

TABLE XI

VALUES OF ϵ_1 , C, AND T_c FOR VARIOUS CATION
SUBSTITUTIONS IN THE SrTiO_3 STRUCTURE

(After Table 2, Section 5.1, Report No. 8 of This Series)

<u>Material</u>	<u>ϵ_1</u>	<u>C, °K</u>	<u>T_c, °K</u>
SrTiO_3	43.0	7.1×10^4	37
$\text{Ca}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$	39.0	6.56×10^4	-12
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	45.2	7.47×10^4	227
BaTiO_3	44.2	12.0×10^4	395
CaTiO_3	58.0	4.19×10^4	-84
KTaO_3	45.8	5.72×10^4	7

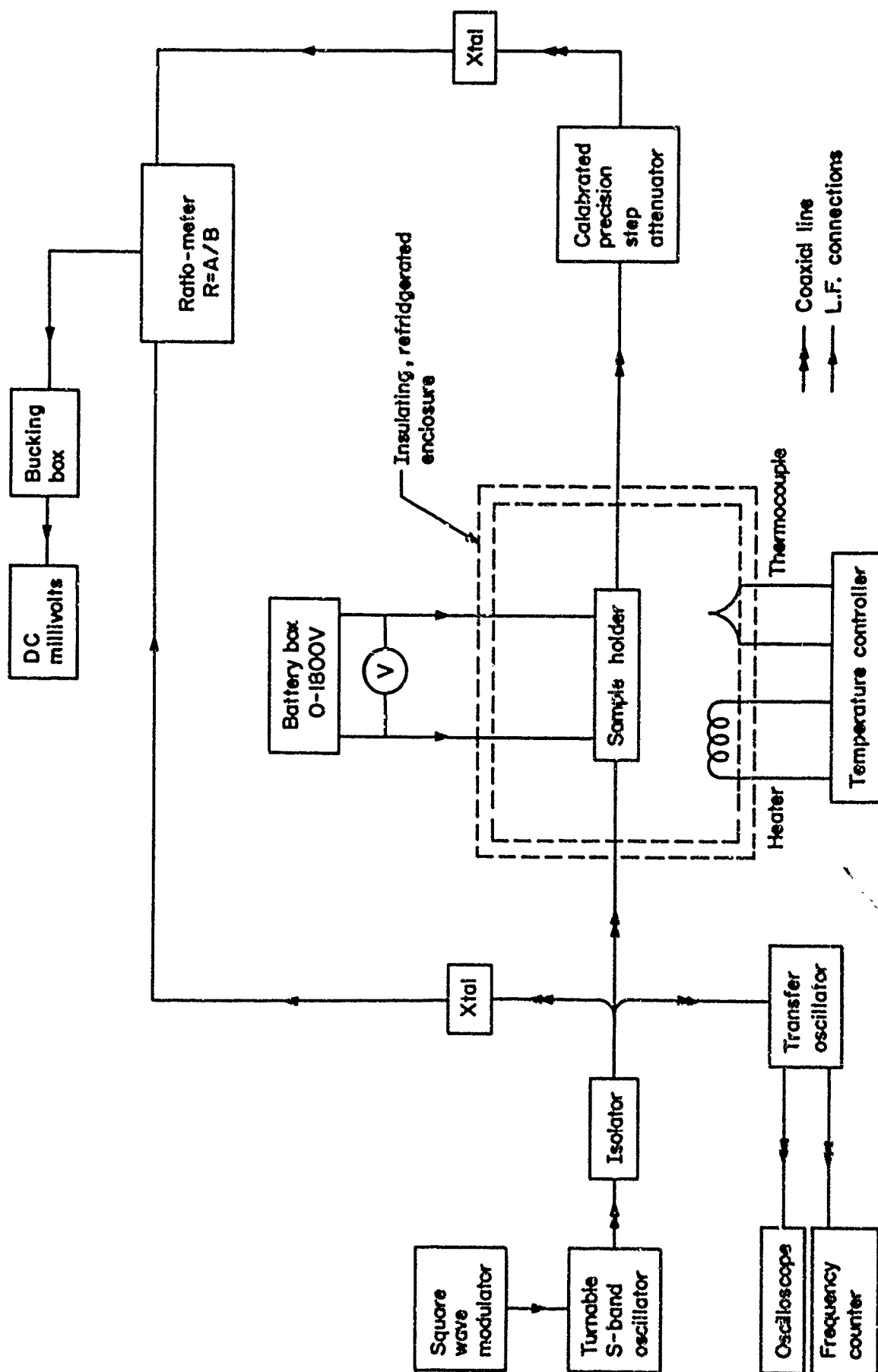
Figure 2 shows the schematic diagram of the field-dependent loss measurement apparatus. The single-crystal SrTiO_3 sample was mounted in a slab line configuration⁸ and placed in a coaxial sample holder such that the microwave and dc electric fields were parallel to the $[110]$ direction. Temperature was kept constant (usually at 77°K) and frequency was swept over a sample resonance in the S-band range. Transmission coefficient was read out of the ratio-meter fed by two detecting crystals. Frequency was measured by a counter connected to a transfer oscillator.

Experimentally the peak value of transmission was observed for a given resonance. Then 1 dB of transmission attenuation was taken out by means of the precision step attenuator, and frequency moved either side of the peak until the ratio meter output, as read on the dc millivoltmeter, was the same as previously. Thus a "1 dB" frequency width was determined, and this was related to loss tangent by

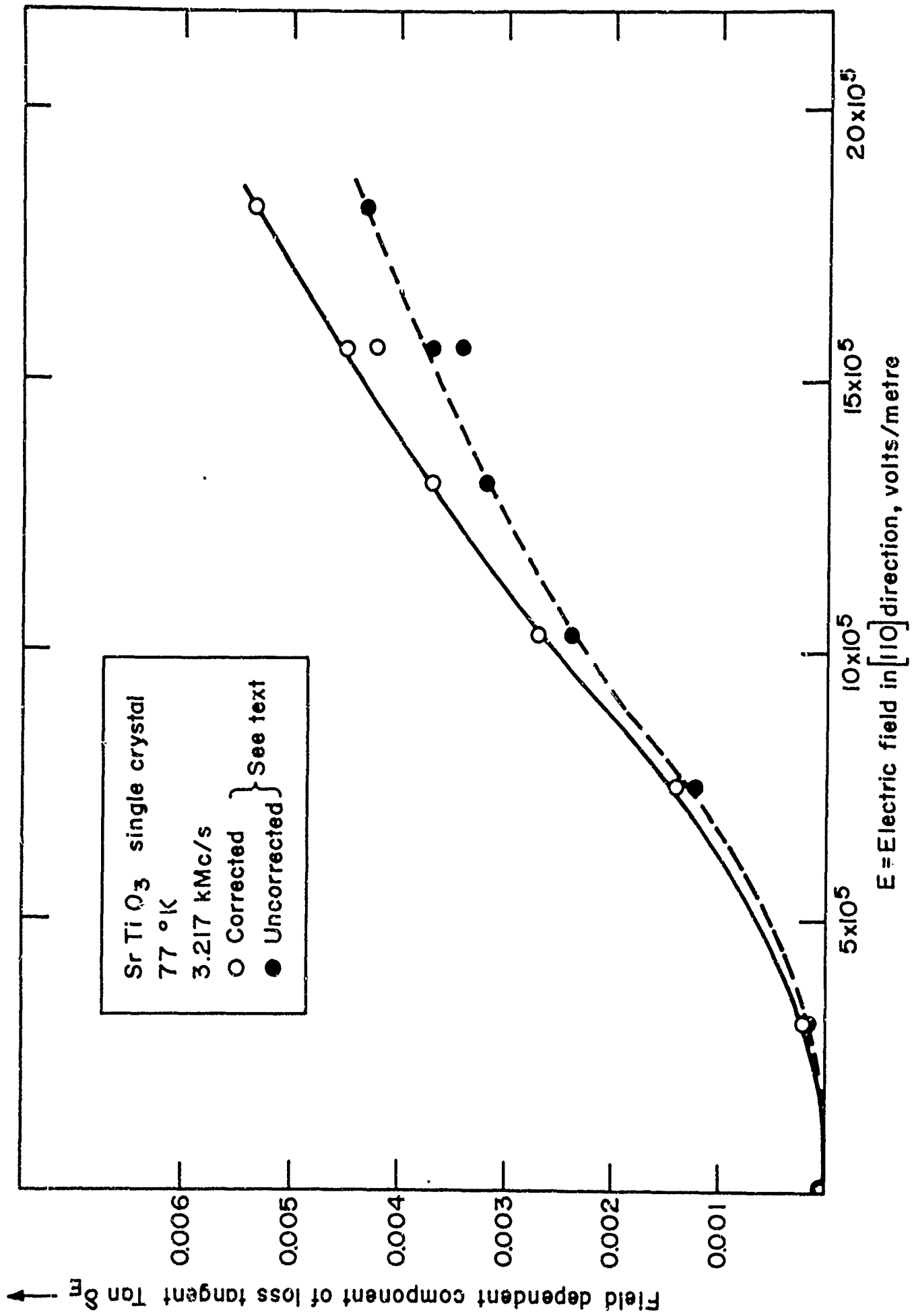
$$\tan \delta_0 = \frac{\Delta f_{3\text{dB}}}{f_0} = 1.96 \times \frac{\Delta f_{1\text{dB}}}{f_0}$$

by assuming a Lorentzian line shape. The measurement was then repeated with an applied field on the sample, giving a value of $(\tan \delta)_E$. The field-dependent loss was then $\tan \delta_E = (\tan \delta)_E - \tan \delta_0$.

The experimental results on $\tan \delta_E$ for SrTiO_3 at 77°K are given in Fig. 3. The "corrected" curve has taken into account the change in resonant frequency f_0 with applied field (due to nonlinearity). This is necessary because both intrinsic sample loss $\tan \delta_0$ and skin loss are functions of frequency.



MEASUREMENT OF FIELD DEPENDENT LOSSES AT S-BAND
FIGURE 2



FIELD DEPENDENT COMPONENT OF LOSS TANGENT VS FIELD FOR SINGLE CRYSTAL STRONTIUM TITANATE

FIGURE 3

6.1.3 September 1962 - September 1963
(Contract No. DA 36-039-SC-89126)

The addition of one mole percent SrSnO_3 to a BST-50 ceramic material had shown³⁷ an enhanced nonlinearity A in 1961-62. It was decided to investigate this phenomenon in more detail⁴⁸ during 1962-63. To this end a new batch of stannate-doped material was made by normal ceramic techniques.⁴⁸ Its nonlinearity A was roughly four times that of an undoped batch of BST 50, while its microwave losses were nearly as low as the best undoped BST-50. These results were very encouraging.

To check the reproducibility of this high nonlinearity, numerous samples of BST-50 + 1% SrSnO_3 were prepared and analyzed.^{49, 50} The material discussed in the previous paragraph was labeled B, and subsequent one percent stannate-doped materials were labeled C, G, and I (actually, materials designated D, E, F, and H were made but exhibited either a spotty surface appearance or low density and were not analyzed). C, G, and I all had nonlinearities about the same or slightly higher than normal BST-50, but none were close to that of sample B, as shown in Table XII. The reduced nonlinearity $\eta(E, T) = [\epsilon(O, T) - \epsilon(E, T)] / \epsilon(E, T)$ replaces A_{hkl} as the measure of nonlinearity in all further work. $\eta(E, T)$ is a convenient device parameter, being essentially the fractional change in E with a given applied field. It is measured at constant temperature. The losses of C, G, and I were those typical of undoped BST-50 or slightly worse.

A great deal of effort was directed at understanding the high nonlinearity of Sample B. First, it was thought that the Sn had been incorporated differently in the various materials.⁵¹ Annealing of sample B halved its reduced nonlinearity η , although subsequent annealings left the nonlinearity about the same.⁵⁰ It was undecided whether this reduction was due to more thorough assimilation of Sn into the BST-50 structure or simply to volatilization of the Sn.

TABLE XII
REDUCED NONLINEARITY AND MICROWAVE LOSS TANGENT
FOR BST-50 + 1% SrSnO₃ MATERIALS MADE IN 1962-63
(Data from references 48, 49, and 50)

<u>Material</u>	<u>η (10^6 V/m)</u>	<u>Tan δ</u>
B	0.12 ($T - T_c = 45^\circ\text{K}$)	0.015 ($T - T_c = 80^\circ\text{K}$)
	0.04 ($T - T_c = 80^\circ\text{K}$)	0.009 ($T - T_c = 230^\circ\text{K}$)
C	0.067 ($T - T_c = 50^\circ\text{K}$)	0.021 ($T - T_c = 80^\circ\text{K}$)
	0.03 ($T - T_c = 75^\circ\text{K}$)	0.014 ($T - T_c = 195^\circ\text{K}$)
		0.013 ($T - T_c = 270^\circ\text{K}$)
G	0.048 ($T - T_c = 60^\circ\text{K}$)	0.014 ($T - T_c = 90^\circ\text{K}$)
	0.018 ($T - T_c = 80^\circ\text{K}$)	0.008 ($T - T_c = 250^\circ\text{K}$)
I	0.055 ($T - T_c = 60^\circ\text{K}$)	-----
	0.022 ($T - T_c = 80^\circ\text{K}$)	-----
<hr/>		
undoped, hot pressed	0.06 ($T - T_c = 45^\circ\text{K}$)	0.017 ($T - T_c = 80^\circ\text{K}$)
	0.025 ($T - T_c = 80^\circ\text{K}$)	0.008 ($T - T_c = 250^\circ\text{K}$)

Secondly, the grain size and other microstructure characteristics of all the one percent stannate-doped BST-50 materials were examined.⁵⁰ They revealed that sample B had somewhat smaller grain size ($\sim 30\mu$) and had fewer voids within the grains themselves. These data were not clear-cut enough to explain the high reduced nonlinearity of sample B, however.

The third possibility was that extraneous impurities had been introduced into the materials through the preparation and milling processes. A spectroscopic analysis of both the B and G materials showed rather large (~ 1 to 2%) aluminum and silicon impurities in both samples, B containing more aluminum and G containing more silicon.⁵¹ As a result of this finding it was decided to attempt an intentional alumina (Al_2O_3) doping in BST-50 and assess its effect upon nonlinearity.

This effect was considerable:⁵² for $(T - T_c) = 85^\circ\text{K}$, the reduced nonlinearity of a five-mole percent alumina-doped BSt-50 turned out to 0.063, while the corresponding figure for the B material had been 0.04 approximately. The alumina-doped BST-50 showed an appreciable dc conductivity, and this problem was to recur occasionally in later batches.

It should be mentioned that three percent stannate substitutions (not merely additions) were made to BST-50, and the nonlinearity was about that of pure BST-50.⁵³

One- and five-mole percent substitutions of SrSnO_3 to SrTiO_3 were made⁵⁴ and their nonlinearities are tabulated in Table XIII. It is clear that the same behavior holds with respect to percent doping in SrTiO_3 as in BST-50 except that the five percent addition is still considerably better than the undoped material. No loss data on these materials are available.

TABLE XIII

NONLINEARITY OF STANNATE-DOPED STRONTIUM TITANATE

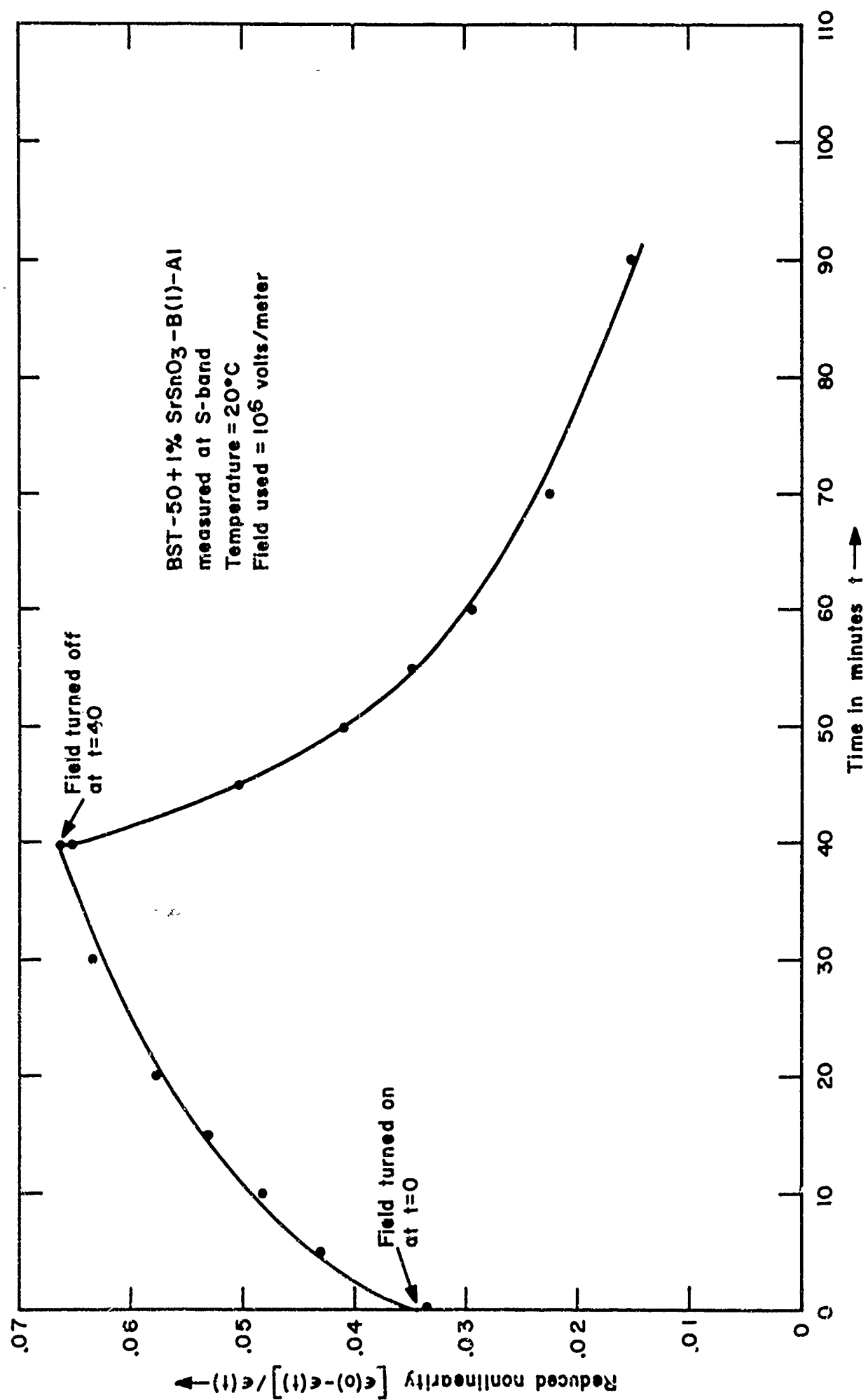
Material	T Temp (°K)	$T - T_c$ Reduced Temp (°K)	$\eta(T, 10^6)$ Reduced Nonlinearity
SrTiO ₃ + 1% SrSnO ₃	77	52	0.155
	120	95	0.030
	140	115	0.010
SrTiO ₃ + 5% SrSnO ₃	77	57	0.053
	120	100	0.012
	140	120	0.008
SrTiO ₃	---	52	0.0392
	---	57	0.0299
	---	95	0.0070
	---	100	0.0060
	---	115	0.0040
	---	120	0.0036

The phenomenon of dielectric constant drift with time upon application of a dc biasing electric field had been observed experimentally on many BST-50 samples (both doped and undoped) during the course of the doping experiments.⁵⁵ This behavior, plotted as reduced nonlinearity versus time $\eta(t) = [\epsilon(0) - \epsilon(t)] / \epsilon(t)$ for a biasing field of 10^6 V/m is plotted for an annealed one percent stannate-doped BST-50 material at 20°C in Fig. 4. Similar data at 40°C showed a considerably faster rise and fall of nonlinearity, but the time dependence was still very marked. The nonlinearity of SrTiO₃, on the other hand, proved much more stable⁵⁶ with time than BST-50.

It should be emphasized that the constant temperature non-linearity measurements taken on the stannate-doped BST-50 and all subsequent samples give the value of nonlinearity corresponding to one minute or less after application of the field. The previous constant frequency method required 5 to 10 minutes to observe the nonlinearity⁵⁷ because of the necessarily slow temperature drift.

The possibility of space charge effects causing this unstable dielectric constant was considered⁵⁸ and rejected on the basis that the space charge would have to extend $\sim 140 \mu$ from an electrode to cause the magnitude of variations observed. No good explanation of the phenomenon was advanced; however, its negative effect on the usefulness of ferro-electric devices should be clear.

The field-dependent losses of SrTiO₃ at x-band in the temperature range 77° - 140°K were again studied, using the differentially chopped bias technique,⁵⁹ which kept temperature constant and swept frequency from 8.0 to 12.4 Gc/sec. The results were in qualitative agreement with those measured during 1961-62.⁴⁷ The new method eliminated errors due to change in coupling with applied field, by using a weakly coupled sample.



TIME-DEPENDANCE OF DIELECTRIC CONSTANT WITH STEADY APPLIED FIELD

FIGURE 4

However, a new phenomenon was observed which not only produced uncertainty in the results but cast doubt upon the usefulness of SrTiO_3 near 77°K as a device material. It was observed at low temperatures that the sample resonances tended to split into two or more peaks as a function both of applied field and time.^{59, 60} This phenomenon had escaped detection previously, probably because the resonant peaks had not been actually traced out as a field was applied.

A proposed explanation of the splitting was that space charge build up near an electrode with time and with field⁶¹. If the SrTiO_3 resistivity were nonuniform, the space charge and internal field would thus be nonuniform. Hence dielectric constant would vary over the sample and this could give rise to splitting. The temperature dependence of the phenomenon ruled out this explanation since SrTiO_3 has a negative temperature coefficient of resistivity, being an insulator, and the effect should be more pronounced at lower resistivity.

An alternate explanation⁶¹ was proposed which assumed that due to sample inhomogeneity certain volumes of material experienced an electric field much higher than the average. It was then assumed⁶² that SrTiO_3 , like BaTiO_3 , could become ferroelectric above its Curie temperature if a strong enough field were applied. Thus small ferroelectric regions would appear in the sample, and, due to their low dielectric constant, would grow by increasing the local field even more. This could result in peak splitting with the observed field and temperature dependence.

Due to increased interest in the microwave properties of BST-50 in the ferroelectric region, a method was developed⁶³ specifically for measuring the dielectric constant and loss tangent in this region. A circular rod of material was placed at the center of an x-band circular cavity operating in the TM_{030} mode. As the temperature of the cavity and sample was varied, the resonant frequency of the loaded cavity varied due to the temperature dependence of the dielectric constant of BST-50.

The plot of frequency vs temperature was converted to one of dielectric constant vs temperature by means of a calculated solution to the boundary value problem. This calculation assumed a lossless material but was otherwise exact. From the Curie peak upwards in temperature, the data obtained in this way gave excellent agreement with data taken at 1 Mc/sec on the same material. Below the Curie peak, the X-band values were consistently lower than those at 1 Mc/sec. This was thought⁶⁴ to be caused by the assumption of a lossless material in the calculation, but conceivably could reflect a dispersion of dielectric constant somewhere between 1 Mc/sec and ~10 Gc/sec in frequency.

A more general calculation was set up early in the following quarter (see Appendix, Report No. 13) which included the effect of a lossy material. This was never used because (a) the Q of the loaded cavity resonance was very difficult to measure in the ferroelectric region, (b) application of a field to the material (for field-dependent loss measurements) would require rather sophisticated design, and (c) the differentially chopped bias method was found to give the same results with fewer engineering problems.

6.2 The Period September 1963 - September 1964 (Contract No. DA 36-039-AMC-03389(E)) *

During the present contract period, three areas were emphasized: preparation of ceramic materials, continued doping experiments, and measurements on (Ba,Sr)TiO₃ ceramics near the Curie temperature.

It is appropriate to describe first the method by which the bulk of the microwave measurements of dielectric constant, nonlinearity, and loss tangent reported during 1963-64 were taken. It has been mentioned that a cavity loading technique had been used in 1962-63 but was abandoned because of certain practical considerations.^{63, 64}

* Reports No. 13-16 of this Series published under this contract number.

The new technique utilized the nonlinearity of the ferroelectric resonant cavity sample to produce a transmission curve versus frequency which was easily distinguishable from the transmission of the waveguide or coaxial cable system.⁶⁵ This is important because the desired loose coupling of the sample normally makes its transmission nearly indistinguishable from that of the system because of the frequency dependence of flange reflections.

The microwave system was the same as an earlier constant-temperature setup⁴⁷ except that waveguide as well as coaxial cable was used (the choice was merely a matter of convenience). Two significant differences were the sample holder and the method of resonance detection.

The sample holder⁶⁵ afforded a loosely coupled configuration and a convenient means of inserting, temperature controlling, and removing the sample. Detection was carried out by running the microwave source cw and incrementally modulating the sample bias at a 1 kc rate⁶⁵ as frequency was swept either from 1.9-4 Gc/sec or 8.0-12.4 Gc/sec. Hence the designation "differentially chopped bias method." The derivative of the sample transmission versus frequency could be detected since, through the sample nonlinearity, the center frequency of a given resonance was incrementally changed at a 1 kc rate also.

This method of measurement is applicable to high loss materials since only sample resonances are detected. However, if loss tangent becomes extremely high ($\tan \delta \sim 0.5$) or nonlinearity extremely low [$\eta (10^6 \text{ V/m}) \sim 0.01$] or both, the signal will disappear. This fact, plus the necessity of electroding and biasing the sample, are the basic limitations of the differentially chopped bias method. For our work, the convenience of the method overshadowed these limitations.⁶⁵

Due to the scattered results of stannate and alumina doping in SrTiO_3 and BST-50 ceramics, it was thought that impurities introduced in the milling process were influencing the nonlinearity in an uncontrollable manner.⁶⁶ It was further conjectured, and later experimentally shown, that the major source of impurity was the grinding of the milling balls against one another; the milling jar introduced negligible impurity. Milling balls of BST-50 and SrTiO_3 were constructed and used in the milling of the appropriate material.⁶⁷

This method was found to reduce impurity to very low levels.^{67, 68} The reproducibility of microwave nonlinearity among ceramic samples so prepared was improved, but only a few of these materials showed the high nonlinearity previously obtained in a few scattered samples. This result was disappointing not only because of the well-controlled impurity of the samples, but also because of their high density and good mechanical properties. All subsequent ceramics were prepared by milling with balls made of the same material.

A BST-50 sample was fired for 50 hours, rather than the usual 10 hours, so that its grains grew to a size of 20 - 30 microns.⁶⁹ The resultant material was not dense and had unfavorable machining properties. Its nonlinearity near the Curie peak was very high, and several large grain BST-50 and BST-70 materials were made.⁷⁰ These will be elaborated upon at the end of this section.

Another control process was introduced in the preparation of the doped ceramics. Along with each doped sample (or samples) was fired a pellet of undoped material.⁷¹ Thus a control was available by which to measure the effect of the impurity on the sample properties.

The above developments in ceramic preparation techniques stemmed from the desire to optimize the nonlinearity and loss of standard

ferroelectric materials by addition of impurities of a few mole percent. More attention was paid to nonlinearity than to loss because device theory has indicated that device losses can be limited by unavoidable "encapsulation loss."⁷²

Presented below are the central results of the microwave evaluation of ceramic BST-50, BST-70, BaTiO₃ and SrTiO₃ samples produced in 1963-64. It should be noted that as the work progressed, the microwave results had a continuing effect upon the preparation techniques discussed earlier, particularly with respect to the large-grain samples.

Stannate doping of ceramic SrTiO₃ was continued⁷² and the high nonlinearities of previous batches⁵⁴ was not reproduced. It was at this point that doped materials were thenceforth accompanied by the corresponding undoped material during firing.⁷¹ The next three firings of doped and undoped SrTiO₃ were analyzed to show very little dependence of nonlinearity upon stannate doping.⁷³ These results are summarized in Table XIV.

Alumina doping of BST-50 was continued⁷⁴ and at first did not reproduce the high nonlinearity previously reported.⁵² The new material behaved quite differently under applied field from the usual BST-50 behavior,⁷⁴ just as had the old material.⁵² This behavior was partially but not fully restored to normal by baking off the absorbed water.

Five percent alumina-doped BST-50 was prepared⁷⁵ with a control batch of undoped material using the improved ceramics processing.^{67, 71} The nonlinearity of the five percent doped sample was slightly higher than the high value observed originally,⁵² and due to the well-controlled preparation could be confidently ascribed to the alumina doping. As an additional check, a similar batch of alumina doped and analyzed BST-50 ceramic was prepared using the old ceramic techniques⁷⁵ and showed the same nonlinearity as ordinary BST-50. These results are tabulated in Table XV and XVI

TABLE XIV
MICROWAVE PROPERTIES OF STANNATE-DOPED SrTiO₃
(Measured at S-Band)

Sample		C, °K	T _c , °C	η (10 ⁶ V/m)		
				-195°C	-170°C	-160°C
8354-31	0%	6.88 × 10 ⁴	-238	0.066	0.025	0.016
	3%	5.29	-236	0.052	0.040	0.014
	5%	6.06	-235	0.041	0.019	0.010
Calcined 8354-31	0%	6.54	-234	0.083	0.031	0.0175
	2%	6.9	-250	0.045	0.016	0.010
	5%	7.26	-242	0.056	0.021	0.010
8354-32	0%	7.02	-250	0.056	0.019	0.013
	2%	8.22	-247	0.047	0.017	0.014
	5%	7.77	-246	0.057	0.022	0.014

TABLE XV

NONLINEARITY OF ALUMINA-DOPED $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ CERAMICS

(Materials Milled Using BST-50 Balls)

BST-50 Material	T_c , °C	C, °K	η (20°C, 10^6 V/m)
Undoped (64-17)	-19	7.3×10^4	0.106
+ 3% Al_2O_3 (64-16)	-36.5	7.0×10^4	0.106
+ 5% Al_2O_3 (64-15)	-45.5	6.5×10^4	0.129

TABLE XVI

NONLINEARITY OF ALUMINA-DOPED $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ CERAMICS(Materials Milled Using Al_2O_3 Balls)

BST-50 Material	T_c , °C	C, °K	η (20°C, 10^6 V/m)
Undoped (64-3A)	not measured	not measured	0.079
+ 3% Al_2O_3 (64-2A)	-33.7	7.8×10^4	0.070
+ 5% Al_2O_3 (64-1B)	-44.5	4.9×10^4	0.051

This completes the summary of doping experiments for evaluation in the paraelectric region. The qualitative results may be stated as follows. stannate doping of BST-50 in the range of one to three mole percent may increase the nonlinearity by a small amount but so erratically as to introduce doubt as to the real cause; stannate doping in SrTiO_3 does not increase nonlinearity; five mole percent alumina doping in BST-50 does increase nonlinearity by a factor of 1.5 to 4 (generally nearer the former), but results in ceramics of low density with a tendency to crack and absorb water.⁷⁶ The improved ceramic processing techniques tend to give more reproducible results than the previous techniques, particularly with regard to undoped BST-50 and SrTiO_3 .

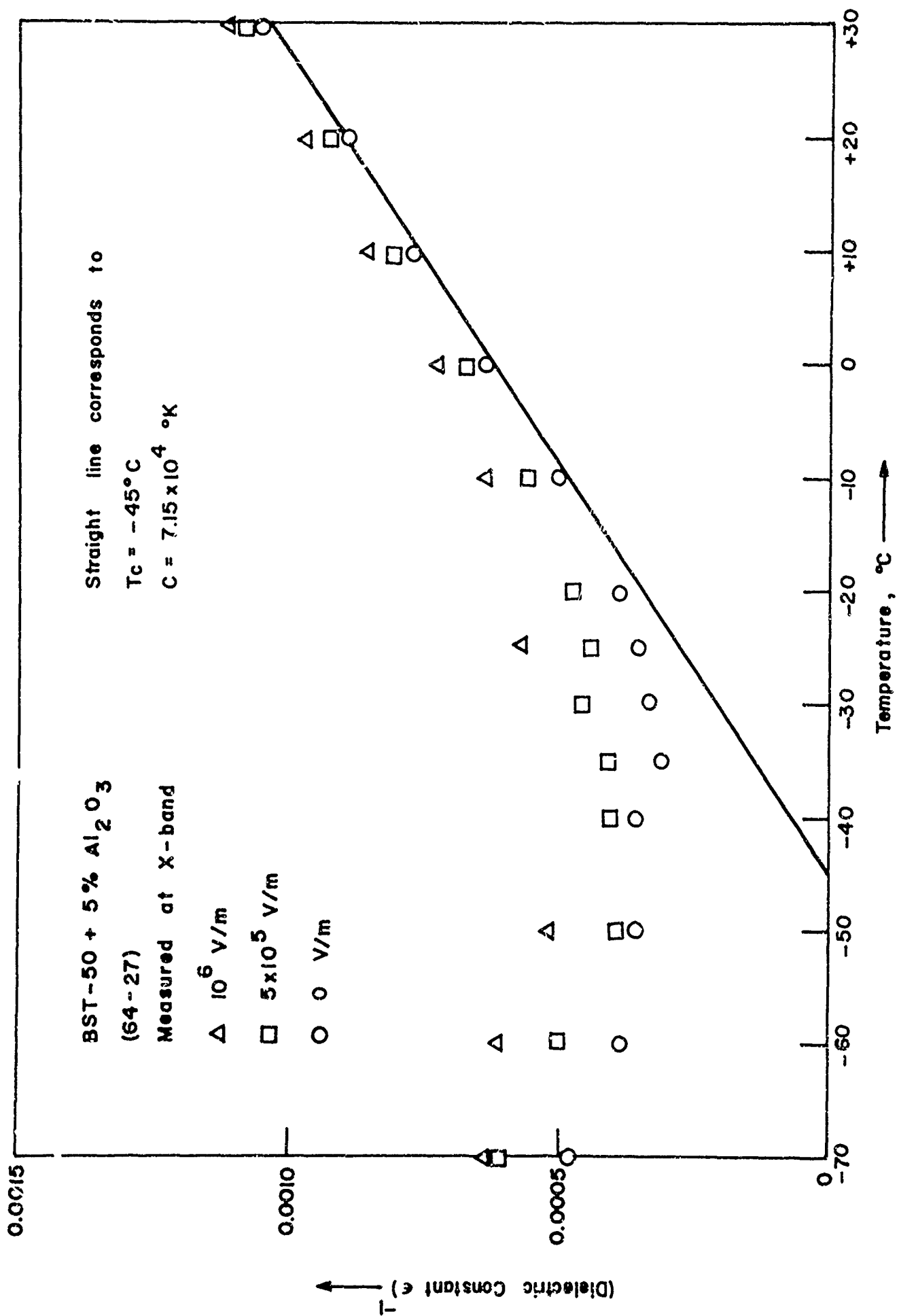
Measurements near T_c of dielectric constant, nonlinearity, and loss tangent of alumina-doped BST-50 ceramics were taken^{77, 78} using the differentially chopped bias technique. This included earlier samples as well as several large grain materials prepared by firing for fifty hours.⁶⁹ Data on the material BST-50 + 5 % Al_2O_3 (64-27), which was not a large grain material, are presented in Figs. 5, 6, and 7. The loss tangent of all these materials is similar to that for sample 64-27, $\pm 25\%$, and was not investigated in any detail. The appropriate data for the large grain materials were similar⁷⁸ except for a higher peak in reduced nonlinearity.

A large grain sample of BST-70 was prepared⁷⁹ and also showed a high peak in nonlinearity vs temperature. A summary of the maximum reduced nonlinearity exhibited by BST-50 and BST-70 alumina doped and undoped samples is presented in Table XVII. Also see Tables I-V of this report.

Near the Curie peak, the nonlinearity increases greatly, as do the losses. The rules for maximizing nonlinearity in this region are not as definite as those for the paraelectric region, but they do seem to be qualitatively different. The amount or type of impurity doping does not

TABLE XVII
SUMMARY OF MEASUREMENTS
IN THE CURIE TEMPERATURE REGION

<u>Material</u>	<u>η_{\max} (10^6 V/m)</u>	<u>T</u>
BST-50 + 0 % Al ₂ O ₃ (No. 64-3)	0.95	-30°C
BST-50 + 0 % Al ₂ O ₃ (No. 64-17)	0.58	-15°C
BST-50 + 3 % Al ₂ O ₃ (No. 64-16)	1.04	-40°C
BST-50 + 5 % Al ₂ O ₃ (No. 64-15)	0.88	-30°C
BST-50 + 5 % Al ₂ O ₃ (No. 64-27)	0.54	-25°C
BST-50 + 0 % Al ₂ O ₃ (8354-33)(large grain)	1.43	-45°C
BST-50 + 5 % Al ₂ O ₃ (8354-33)(large grain)	1.60	-50°C
BST-70 + 0 % Al ₂ O ₃ (8354-38)(large grain)	1.34	+30°C
BST-70 + 5 % Al ₂ O ₃ (8354-38)(large grain)	0.58	+15°C
BST-70 + 0 % Al ₂ O ₃ (8354-47)(large grain)	1.40	+30°C



CURIE PLOT OF DIELECTRIC CONSTANT VS TEMPERATURE FOR ALUMINA
 DOPED BST-50

FIGURE 5

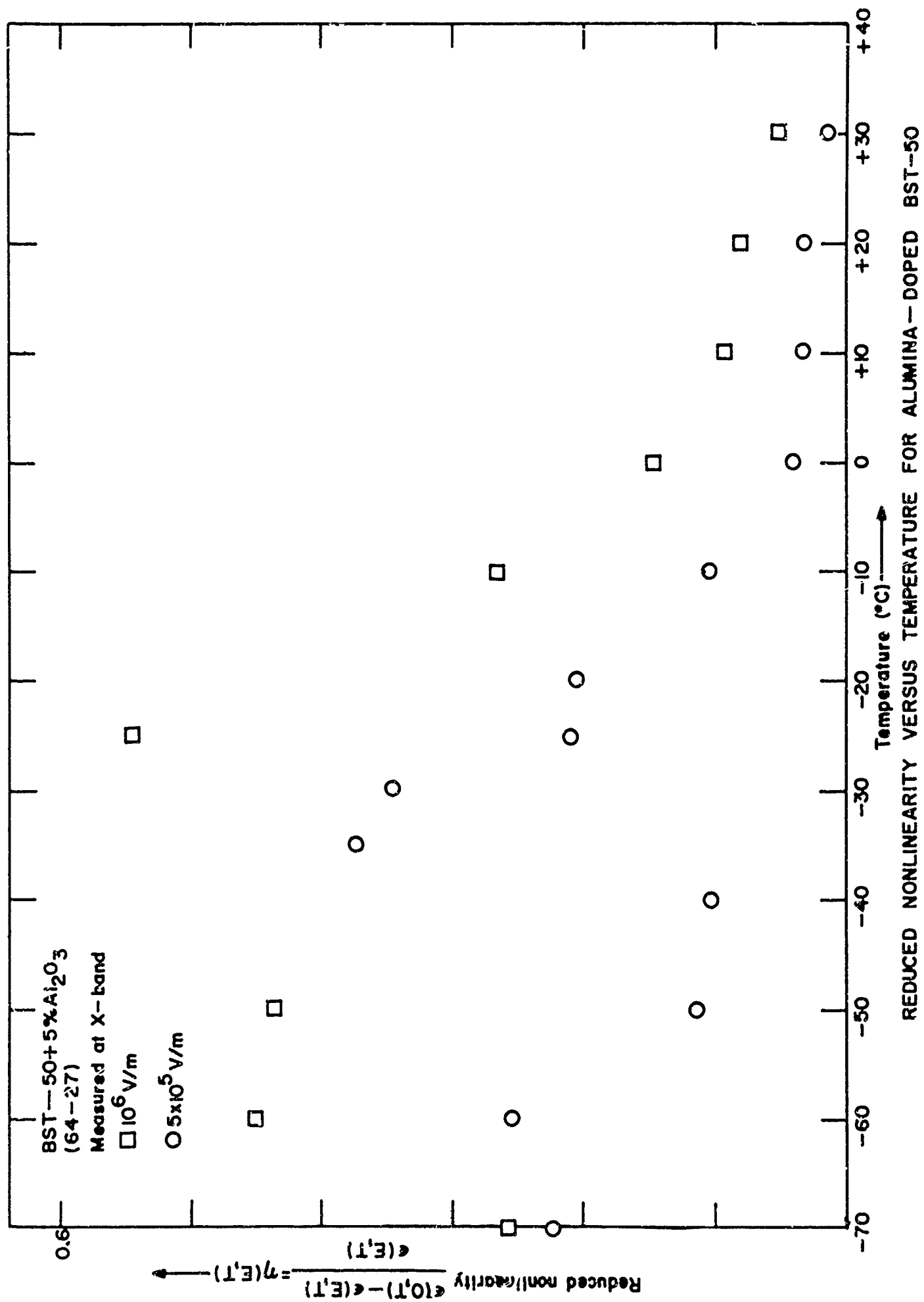
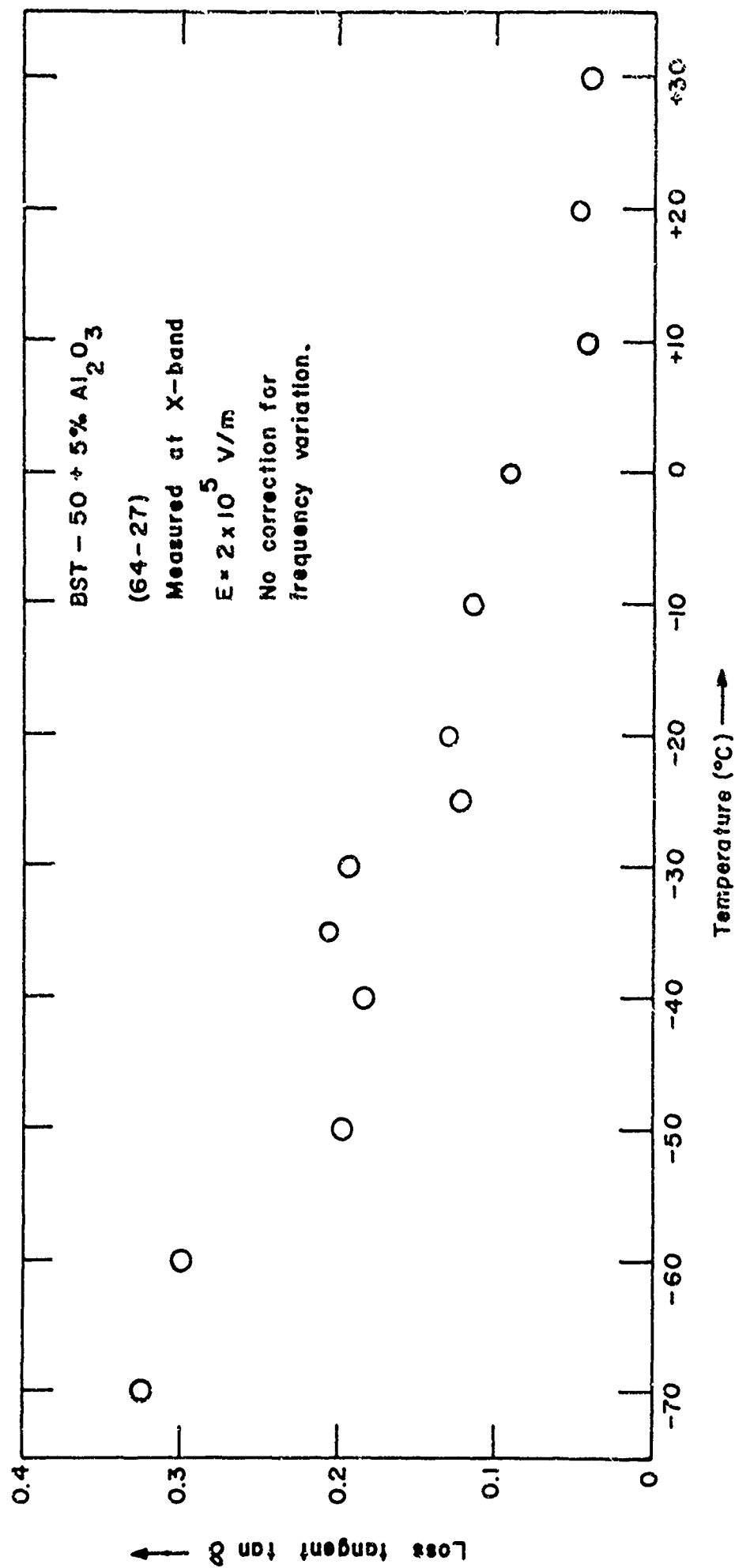


FIGURE 6



X-BAND LOSS TANGENT VS TEMPERATURE FOR ALUMINA - DOPED BST - 50

FIGURE 7

appear to influence nonlinearity in a consistent manner. Large grain size seems to produce an enhancing effect, but has been accompanied by low density and poor machining properties. It is possible to produce dense, hard ceramics of large grain size by means of hot pressing, but this work has not been pursued during the present contract period.

It is not surprising that factors influencing the nonlinearity change as the temperature is lowered from the paraelectric region to the ferroelectric. In the former case, size or valency mismatch of impurities disturb the lattice potential seen by the cation.

Near the transition in ferroelectric ceramics, field-induced transitions may play the major role in producing nonlinearity, as Diamond⁵ has suggested. Evidently, impurities have little effect on the ease with which a transition is induced by the field. The large grain size and porosity of certain samples may produce local macroscopic field concentrations which do encourage the induced transitions. If this simple theory is correct, then hot pressing to produce dense sample of large grain size may well reduce the nonlinearity in the Curie peak region.

The high nonlinearities observed in the Curie region would be acceptable for a ferroelectric device if accompanied by a reasonably low loss tangent ($\tan \delta \sim 0.05$ to 0.1 for example). However, measurements of $\tan \delta$ vs frequency for BaTiO_3 , BST-50 and BST-70 in the Curie peak region showed that the S-band losses (2-4 Gc/sec) are about as high or higher than the X-band losses (8-12 Gc/sec).⁸⁰ This result is in contrast to earlier measurements in SrTiO_3 well above T_c , in which the frequency dependence of $\tan \delta$ was found to be linear.⁵

The cause of the loss vs frequency behavior may be a relaxation in the dielectric constant somewhere in the microwave region. Stanford has already found evidence for such a relaxation.⁸¹ Whatever the cause, the end result of these measurements is indeed disappointing from the standpoint of device applications.

Dopings of BaTiO_3 with one-half, one, and two mole percent of lanthana (La_2O_3) was undertaken to make use of the drastic lowering of the Curie temperature of the material which lanthana is known to cause. The hope was that a nearly pure (unmixed) perovskite material could be obtained with a Curie point near room temperature. With all these samples, except one, no signal was observed in the microwave test setup over a wide temperature range.* A two percent lanthana-doped BaTiO_3 sample was successfully analyzed, but its properties were disappointing.

*-----
* This implies either a low nonlinearity or high loss tangent, as mentioned on p. 45.

6.3 Over-all Conclusions

The stated purpose of the work of the last four years is to develop and investigate those materials showing high nonlinearity, low loss, and low dielectric constant suitable for microwave device applications. More specifically, the contract goal was a material showing:

- A. Variation of dielectric constant of 50 percent with an applied field of 10^6 V/m.
- B. $\tan \delta \leq 0.002$.
- C. Dielectric constant as low as possible, a single-valued function of applied field, and varying not more than ± 10 percent from -55°C to $+85^\circ\text{C}$.

The restriction on loss tangent $\tan \delta$ has been unofficially loosened because of encapsulation loss inherent in microwave devices. In addition, devices usually accommodate a "trade-off" between loss and nonlinearity; i. e., if nonlinearity is exceptionally high, somewhat higher losses can be tolerated. A maximum tolerable loss tangent of 0.050 is a reasonable goal (if nonlinearity satisfies condition A). No material yet investigated satisfies both these requirements.

Ignoring the loss tangent requirement, let us look at Requirement A. Numerous mixed (Ba, Sr) TiO_3 ceramics have equalled or exceeded the nonlinearity requirements ($\eta(10^6 \text{ V/m}) \geq 1$) in a limited temperature range near the Curie peak. No material has even approached this value of η at, say, 50°C above the Curie peak, where the temperature dependence might be tolerably low. Several ferroelectric materials (operating below T_c) have shown nonlinearities approaching but in no case exceeding 1. In this range the dielectric constant temperature dependence is suitably weak but the losses are prohibitively high ($\tan \delta \sim 0.3$ to 0.4). It should be emphasized that ferroelectric materials satisfying $\eta(10^6 \text{ V/m}) \sim 1$ are rare; most materials are characterized by values from 0.2 to 0.5. Hence this avenue would not appear to be a very desirable one to explore, even ignoring losses.

While the single-valuedness of dielectric constant with applied field appears to hold for mixed perovskite ceramics, there exists a time dependence of the order of 10 to 20 percent in the nonlinearity upon application of a field. This variation extends over a period of perhaps one-half hour and could be a definite hindrance to device applications.

It would appear that no ferroelectric (or paraelectric) material of the types studied in this laboratory will achieve the contract goals. Qualitatively, when one property has been improved, another property has deteriorated. Further variations of mixed perovskite ceramics or single crystals offer little hope of a major improvement, which is imperative if successful devices are to be made.

Other categories of materials than perovskite ferroelectrics have not been studied in this work. Aside from the well-known varactor based on a back biased semiconductor junction, two types of materials suggest themselves. The first consists of materials such as KH_2PO_4 (KDP) in which hydrogen bonds, rather than interaction between oxygen and titanium sublattices, give rise to ferroelectricity. The second consists of powdered ferroelectrics materials embedded in an inert binder such as polystyrene. There is, however, no a priori reason to believe that either type of material would prove superior to those already investigated.

7. ACKNOWLEDGMENTS

We wish to acknowledge the careful work of B. Wilson in taking the microwave measurements reported here.

We are also indebted to J. Molloy for fabricating the ceramic samples used in this work.

8. IDENTIFICATION OF PERSONNEL

Hours worked by key personnel during this quarter:

	<u>Hours</u>
P. B. Nutter - Principal Research Scientist	28
A. Paladino - Senior Research Scientist	94
J. S. Waugh - Senior Research Scientist	264
M. Harris - Research Scientist	<u>488</u>
Total	874

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21. Report No. 1 of this series, Section 4.3.5.
22. Report No. 3 of this series, Section 4.2.1.
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56. See Report No. 12 of this series, Section 4.5.
57. See Report No. 11 of this series, Section 5.3.
58. See Report No. 10 of this series, Section 5.5.
59. See Report No. 11 of this series, Section 4.4. Also see Section 5.2 of this report for details.
60. See Report No. 12 of this series, Section 4.4.
61. See Report No. 12 of this series, Section 5.2.

62. There was and is still at this time controversy as to whether SrTiO_3 ever becomes ferroelectric. A recent paper by F.W. Lytle, "X-Ray Diffractometry of Low-Temperature Phase Transformations in Strontium Titanate," J. Appl. Phys. 35, 2212 (1964) indicates a tetragonal phase from 65° to 100°K (with $c/a = 1.00056$). This in itself does not prove that SrTiO_3 is ferroelectric, but does indicate its possibility. For further reference on this subject, the reader is referred to Megaw's book Ferroelectricity in Crystals (Methuen and Company, 1957), Chap. 5. Also see Jona and Shirane, Ferroelectric Crystals (Macmillan Company, New York, 1962), Chap. V, Sec. 8.
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